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## Modification of softwood kraft pulp with carboxymethyl cellulose and cationic surfactants

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**Abstract** An elemental chlorine-free (ECF)-bleached softwood kraft pulp was treated first with a carboxymethyl cellulose (CMC, degree of substitution 0.3, 1% on pulp) and then with alkyltrimethylammonium bromides (alkyl chain lengths of C<sub>10</sub> to C<sub>16</sub>). Surprisingly, the treatment with dodecyltrimethylammonium bromide (C<sub>12</sub>TAB) markedly increased the internal and tensile strengths of the handsheets prepared from the modified pulp. Environmental scanning electron microscopy (ESEM) showed that these properties could be partly explained by the “rope/gum-like” bridges that were formed between the fibers.

**Key words** Surface modification of softwood kraft pulp · Carboxymethyl cellulose (CMC) · Cationic surfactants · Sheet and fiber properties · Environmental scanning electron microscopy (ESEM)

### Introduction

Sodium carboxymethyl cellulose (NaCMC or more commonly CMC) is an anionic polyelectrolyte derived from cellulose and one of the most important cellulose derivatives. In papermaking CMC is used as a wet-end additive, for surface sizing, and as a component of coating colors.<sup>1</sup> Anionic polyelectrolytes do not generally attach on cellulosic fibers because of the electrostatic repulsion between the negatively charged cellulosic surfaces and the anionic polyelectrolyte. Previous studies conducted in this laboratory have showed that CMC grades with a low degree of substitution (DS) are irreversibly sorbed on the external surface of chemical wood pulps<sup>2–4</sup> in the same way as wood xylans.<sup>5,6</sup> The amount of CMC sorbed on pulp depended on several factors, including the degree of polymerization

(DP), DS and charge of the CMC, pH and ionic strength of the sorption medium, and the beating level of the pulp.<sup>2</sup> The sorption of CMC on cellulose pulps improved the strength properties of handsheets,<sup>3</sup> because the CMC treatment greatly increased the interfiber bonding in handsheets. Because CMC may adopt a similar chain conformation with crystalline cellulose, the sorption of CMC with a low DS is probably enabled by this conformational change, as in the case of wood xylans.<sup>5,6</sup> Later, other studies<sup>7</sup> have shown that the sorption of CMC with a higher DS can be enhanced by adding a calcium salt.

CMC is a polyelectrolyte and polyelectrolytes tend to form micellar aggregates or micelle-like clusters with surfactants of opposite charge. The present understanding of polymer–surfactant interactions in aqueous solution has been summarized in several reviews.<sup>8–10</sup> For CMC, the driving force of the aggregation (cooperative) of cationic surfactants with CMC has been found to be of electrostatic and hydrophobic origin, that is, the association was strengthened as the hydrophobic chain length of the surfactant or the charge density of the polysaccharide increased.<sup>11,12</sup> In general, the cooperativity also depends on the other features of the polyelectrolyte, such as the flexibility of the chains and the hydrophobic character of the repeating unit.<sup>13,14</sup> An added electrolyte in the polyelectrolyte–surfactant system makes the electrostatic interactions less important and thus weakens the attraction between the polymer and the surfactant.<sup>8,15</sup> Addition of salt can also stabilize the surfactant aggregates or it may, on the other hand, induce the growth of micellar aggregates, thus leading to initiation of interpolymer complexes.<sup>16</sup> Interactions between CMC and cationic surfactants have been studied in the presence and absence of salts, showing the interaction to be strongly cooperative in nature.<sup>17</sup> The effect of a nonionic surfactant on the CMC–cationic surfactant system has also been studied.<sup>12</sup>

Although CMC and surfactants are well-known chemicals in the pulp and papermaking industry, only a few attempts have been made to study the combined effect of CMC and surfactants on paper properties. The present study examines the surprising effects of cationic surfactants

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(alkyltrimethylammonium bromides) on the papermaking properties of a softwood pulp modified with CMC. The structures of the handsheets were further investigated by environmental scanning electron microscopy (ESEM).

## Materials and methods

### Pulp

The experiments were carried out with an industrial elemental chlorine-free (ECF)-bleached spruce (*Picea abies*) kraft pulp. The pulp was obtained in the form of dry pulp sheets from a mill. The pulp was soaked in water and disintegrated (ISO 5263-1) and then refined (2000 revolutions) in a PFI mill (ISO 5264-2).

### Carboxymethyl cellulose

The commercial CMC sample, Nymcel ZSB-16, was obtained from Noviant. The degree of substitution was 0.32 and the degree of polymerization ( $DP_v$ ) was 700 for the CMC grade used.

### Sorption of CMC on pulp

Because the CMC grades applied were partly insoluble in water, stock CMC solutions (<10 g/l) were prepared in 2.5 M sodium hydroxide. The refined pulp was mixed with water and the stock CMC solution to obtain a final pulp consistency of 5% (50 g/l) and an initial CMC concentration of 0.5 g/l (1% on pulp).<sup>2</sup> The sorptions (pH 12.5) were carried out in glass beakers. The temperature was raised to 60°C in 10 min. After 60 min, the pulp samples were cooled, filtered, and washed with deionized water.

Samples of the liquid phase were withdrawn (about 100 ml) after the sorption, filtered with 0.2- $\mu$ m membranes and then analyzed for dissolved carbohydrates by the phenol-sulfuric acid test.<sup>18</sup> The reference pulps were treated under similar conditions but without CMC. Thus, the results of the phenol-sulfuric acid test were corrected for polysaccharides other than CMC. Two reference and CMC-sorption batches were prepared.

### Sorption of surfactant on pulp

The pulp was modified as described above. The surfactants used in the experiments were alkyltrimethylammonium bromides [ $C_nH_{2n+1}N(CH_3)_3Br$ , where  $n = 10, 12, 14$ , and 16, denotes  $C_{10}TAB$ ,  $C_{12}TAB$ ,  $C_{14}TAB$ , and  $C_{16}TAB$ , respectively) from Fluka and were used without further purification. The surfactant concentration in the diluted pulp suspension before sheet making was 0.02%–0.2% on fibers. Sorption experiments were also carried out with addition of sodium chloride (0.05 M NaCl). After electrolyte and surfactant addition, the pulp was allowed to stabilize for 1 h.

### Papermaking properties

The laboratory sheets were prepared by the standard method ISO 5269-1, with the exception of wet pressing at  $490 \pm 20$  kPa (4 min) and drying in a drum dryer at 60°C for 2 h. The handsheets were prepared in deionized water at a temperature of about 10°C.

The grammage of the sheets was determined by standard method ISO 536, density and thickness according to ISO 534. The light-scattering coefficient was measured with an Elrepho reflectometer by standard method ISO 5631. The tensile strength of the laboratory sheets was determined with a tensile testing machine (MTS 400 M) according to SCAN-P 38:80. Tearing resistance (out-of-plane tear, Elmendorf) was determined according to the standard method ISO 1974. Bonding ability (internal strength) was measured according to Tappi 833 pm-94.

### Environmental scanning electron microscopy

Environmental scanning electron microscopy (ESEM) images of the paper sheets were taken with an ElectroScan ESEM 2020 instrument.<sup>19</sup> The images were taken in the ESEM mode with a gaseous secondary electron detector (GSED) at a temperature of about 23°C. Low-acceleration voltage (10 kV) was used to prevent degradation of cellulose.<sup>20</sup> The pressure in the chamber was 5 torr, the condenser lens setting was 40%, and magnification was 500–1000 times.

### X-Ray photoelectron spectroscopy

X-Ray photoelectron spectroscopy analysis (XPS) measurements were performed with a Kratos Analytical AXIS 165 electron spectrometer using a monochromated Al  $K\alpha$  X-ray source. In order to average over the heterogeneity of the sample, survey scans and high-resolution regional spectra were recorded from at least three measurement points in each sample. All spectra were collected at an electron take-off angle of 90° from sample areas less than 1 mm in diameter. The experimental procedure has been described in more detail by Johansson et al.<sup>21</sup>

### Contact angle measurements

Contact angle measurements of single pulp fibers (Wilhelmy technique) were carried out using a modification of the method described by Hodgson and Berg.<sup>22</sup> The fibers were suspended in the liquid–air interface from a KSV Sigma 70 tensiometer connected to a microcomputer. Twelve generally straight and undamaged fibers per sample were selected and folded at one end into a thin sheet of aluminum. The force acting on the fiber as it advanced and receded through a liquid interface was recorded automatically as a function of the depth of immersion. The solvent probe was water (ultra-high-quality water, UHQ) and was used to calculate the surface tension. The measured surface tension

was  $71.8 \pm 0.5$  mN/m.<sup>23</sup> The maximum immersion depth was 0.7 mm and the velocity 0.9 mm/min. Measurements were carried out in an air-conditioned cabinet at room temperature. Three measurements were performed on each fiber. The method is described in more detail in the reports by Koljonen and Stenius<sup>23</sup> and Laine et al.<sup>24</sup>

## Results and discussion

### Sorption of CMC on pulp

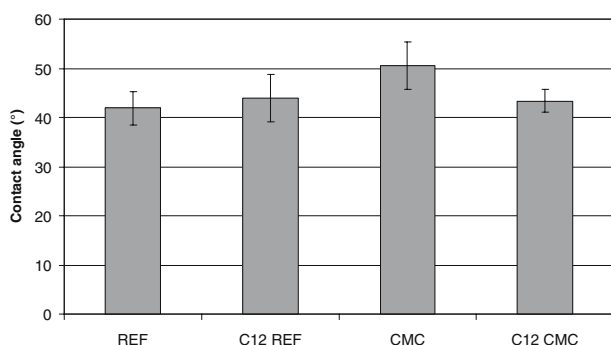
The degree of sorption of CMC on pulp was evaluated by estimating the content of CMC in the sorption liquid by the phenol–sulfuric acid test. Most of the CMC added (approximately 80%) was sorbed on the beaten softwood pulp fibers.

### Fiber properties of pulps treated with CMC

The contact angles for single fibers were measured for the CMC-surfactant-modified and reference pulps (Fig. 1). All the fibers measured were hydrophilic. The variation between different samples, however, was within the experimental error. The contact angle values for the unmodified spruce kraft pulp (REF in Fig. 1) agree quite well with the values reported by Koljonen and Stenius.<sup>23</sup>

### Sheet properties of pulps treated with CMC

Detailed sheet properties of the pulps treated with CMC and alkyltrimethylammonium bromide surfactants, with alkyl chains of C<sub>10</sub>TAB, C<sub>12</sub>TAB, C<sub>14</sub>TAB, C<sub>16</sub>TAB, and of the corresponding reference pulps are illustrated in Appendix 1. The bonding strength (internal strength, tensile strength) and sheet density increased when the pulps were treated with CMC and some of the surfactants in water. In contrast, the tear strength decreased when the pulps were modified with CMC and the surfactants.

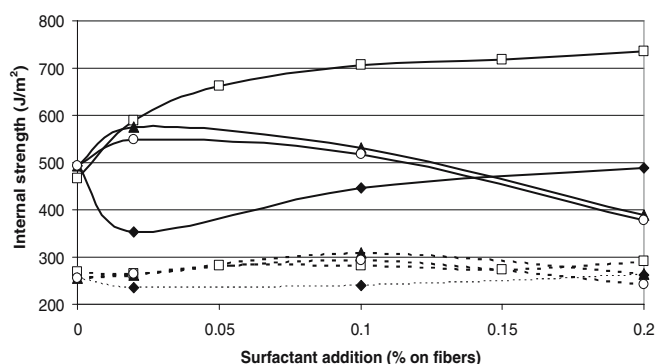


**Fig. 1.** Contact angles of single beaten (PFI 2000) fibers using water as solvent probe. *REF*, reference fibers; *C12REF*, reference fibers treated with 0.1% C<sub>12</sub> trimethylammonium bromide (TAB); *CMC*, fibers treated with carboxymethyl cellulose [addition 1% on fibers, degree of substitution (DS) 0.32]; *C12CMC*, fibers treated with carboxymethyl cellulose and C<sub>12</sub>TAB

The internal strength increased the most when the surfactant C<sub>12</sub>TAB (dodecyltrimethylammonium bromide, C<sub>12</sub>H<sub>34</sub>BrN) was added (Fig. 2). Half of the maximum increase in internal strength was achieved only after adding 0.02% surfactant on fibers. Over 0.05% surfactant addition on fibers did not improve the sheet properties further, but caused foaming in sheet making. Meanwhile, when the surfactants C<sub>14</sub>TAB and C<sub>16</sub>TAB were added, the internal strength initially increased in the same way as for C<sub>12</sub>TAB but started to drop dramatically after adding 0.1% surfactant on fibers. For the reference pulps, the surfactant treatment did not improve the internal strength values at all.

According to the study by Barck and Stenius,<sup>11</sup> the association of the surfactant with the polymer chain increases when the chain length of the surfactant increases. In other words, this could explain in our case why the internal strength values of C<sub>10</sub>TAB are so low (under the critical association concentration). Other properties also influence the association between surfactant and polymer, such as the charge density of the polyelectrolyte and the addition of electrolyte. However, none of these properties influencing the association between surfactant and polymer explains why C<sub>12</sub>TAB gives the highest internal strength values (Figs. 2 and 3).

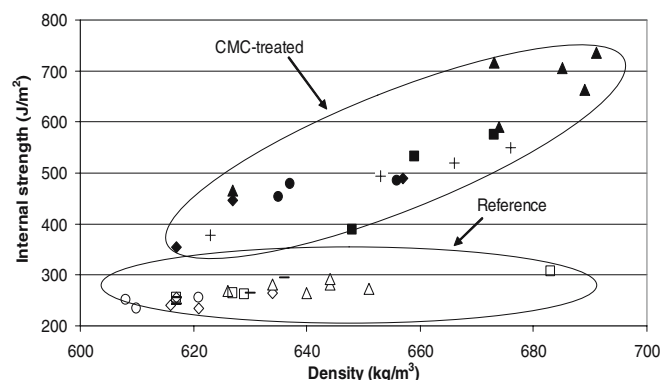
A trend in papermaking is toward increased recycling of drainage waters; hence, there is growing interest in knowing what effects the higher electrolyte concentrations have on paper properties. Therefore, the effect of an electrolyte on the sheet formation was investigated by preparing the laboratory sheets in water and in dilute solutions of sodium chloride (0.05 M NaCl). The internal strengths of the CMC-treated pulps were much higher than those of the corresponding reference pulps (Fig. 2). When the handsheets were prepared from slurries of C<sub>12</sub>TAB-CMC-treated pulp fibers in the presence of sodium chloride, the strength properties dropped to the same level as for the other surfactants (C<sub>10</sub>TAB, C<sub>14</sub>TAB, C<sub>16</sub>TAB), as can be seen in Fig. 3. Meanwhile, the density was clearly decreased and almost all the positive effects of adding the surfactants gained in water were eliminated when salt was added before sheet making



**Fig. 2.** Effect of surfactant addition (C<sub>10</sub>TAB, C<sub>12</sub>TAB, C<sub>14</sub>TAB, C<sub>16</sub>TAB) on internal strength of handsheets from beaten (PFI 2000) pulps treated with carboxymethyl cellulose (CMC) (1%, pH 12.5, DS 0.32). *Solid lines* denote the CMC-treated pulps, *dashed lines* denote reference pulps. *Filled diamonds*, C<sub>10</sub>TAB; *open squares*, C<sub>12</sub>TAB; *filled triangles*, C<sub>14</sub>TAB; *open circles*, C<sub>16</sub>TAB

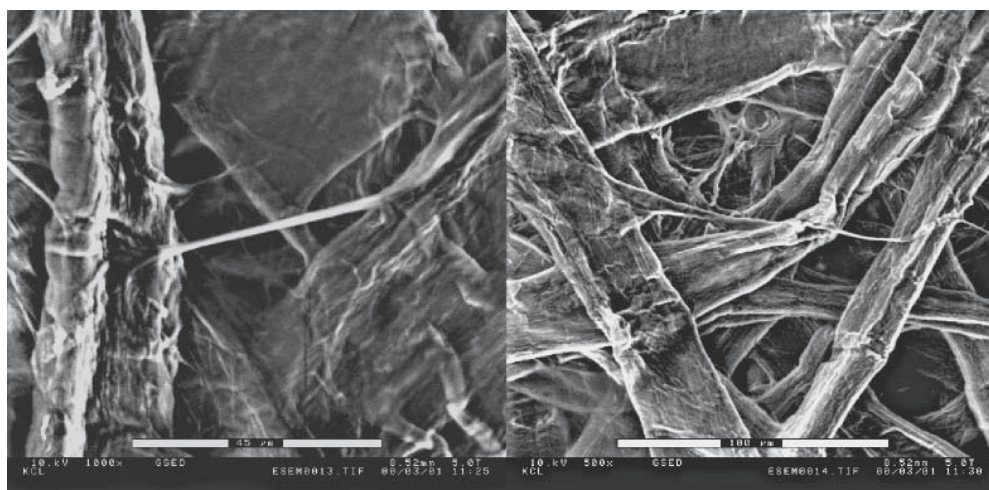
(Appendix 1 and Fig. 3). However, the density was not as sensitive to the electrolyte addition as it was in the studies of Mitikka-Eklund et al.<sup>2</sup> and Blomstedt et al.<sup>3</sup> Furthermore, the addition of CMC increased the internal strength when the comparison was made at a constant density, as shown in Fig. 3. Meanwhile, all the reference samples were gathered in the same cluster, with internal strengths below 300 J/m<sup>2</sup>.

Only a few attempts have been made to study the effect of surfactants on paper properties. The main effect of adding surfactants to mechanical and chemical pulps<sup>25,26</sup> and sulfite pulp<sup>27</sup> was a decrease in strength properties. In most studies, the light-scattering coefficient increased when surfactants were added, although our study showed a slight decrease in the light-scattering coefficient when the pulp was surfactant-CMC-modified. The interactions between surface-active substances and sulfite and sulfate pulps are discussed in the report by Friberg et al.<sup>28</sup> More recently,



**Fig. 3.** Relationship between internal strength and sheet density for beaten (PFI 2000) pulps treated with CMC (addition 1%, pH 12.5, DS 0.32), electrolyte (0.05 M sodium chloride), and surfactants ( $C_{10}$ TAB,  $C_{12}$ TAB,  $C_{14}$ TAB,  $C_{16}$ TAB). Open diamonds,  $C_{10}$  reference; filled diamonds,  $C_{10}$  CMC; open triangles,  $C_{12}$  reference; filled triangles,  $C_{12}$  CMC; open squares,  $C_{14}$  reference; filled squares,  $C_{14}$  CMC; dashes,  $C_{16}$  reference; plus signs,  $C_{16}$  CMC; open circles,  $C_{12}$  reference with electrolyte; filled circles,  $C_{12}$  CMC with electrolyte

**Fig. 4.** Environmental scanning electron microscopy (ESEM) images of handsheets prepared from a beaten (2000 revolutions) and CMC-treated (addition 1%, DS 0.32) pulp sheeted in water when 0.1%  $C_{12}$ TAB was added on fibers. Strong rope-like fibril bridges between the fibers are visible in both images



Alila and coworkers<sup>29</sup> studied the surface charge effects of adsorption of a cationic surfactant onto cellulosic fibers.

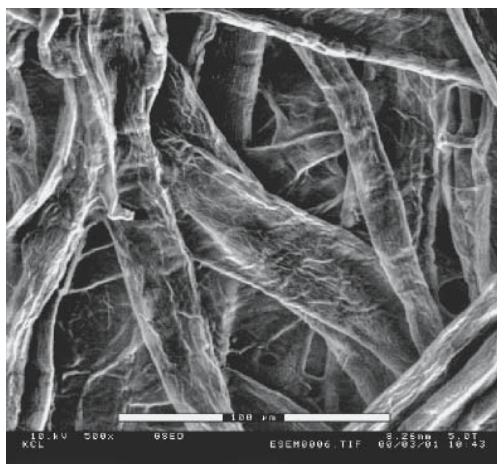
To shed more light on the superior sheet properties presented above, the structure of the sheets was investigated by ESEM. When the surfactant ( $C_{12}$ TAB) was added in the sheet-making stage, the ESEM images of the sheets showed strong “gum/rope-like” fibril bridges between the fibers (Fig. 4). These strong bridges may at least partly explain the improved strength properties of the handsheets prepared. In contrast, the reference sheets were very clean and bridges were hard to find on the surface of the fibers (Fig. 5).

Previous studies in our laboratory<sup>2,3</sup> have examined fibers treated with CMC in the presence and absence of salt with the aid of ESEM. To summarize, the ESEM images clearly showed that each added chemical created different types of bonds between fibers. The addition of CMC created a smooth (chemical) “membrane” on top of the fibers, forming a net of long bridges between fibers.<sup>2,3</sup> In contrast, addition of a surfactant created long and resilient bridges between the fibers (Fig. 4). Furthermore, in most of the images, the bridges caused by addition of the surfactant are linked to the fibers by a multipillared foot.

The surface contents of the cationic surfactants were estimated to be about 2%–6% when analyzed by XPS (Table 1). The surfactants were clearly enriched on the surface, their surface coverage increasing with the chain length of the surfactant. Meanwhile, no actual correlation was seen between the XPS results and the internal strength on the handsheets.

One important thing to remember is that CMC is first permanently attached on the surface of the fibers and then the surfactants are added. Therefore, it is very unlikely that a CMC–surfactant phase does exist in this fiber–CMC–surfactant system. Both cellulose and CMC polymer chains are quite stiff. Therefore, it is improbable that any micellar aggregates are formed in the fiber–CMC–surfactant system. One theory could be that the surfactants (alkyltrimethylammonium bromides) associate with CMC on the anionic fiber surface by ionic and hydrophobic interactions. However, further research is needed to clarify the interaction in the fiber–CMC–surfactant system.





**Fig. 5.** ESEM image of a handsheet prepared from a beaten (2000 revolutions) and CMC-treated (addition 1%, DS 0.32) pulp sheeted in water with no surfactant added. Typical of the sheet are a clean fiber surface and only a few fibril bridges on the surface of the fibers

**Table 1.** X-Ray photoelectron spectroscopy results for pulp treated with carboxymethyl cellulose (CMC) and cationic surfactants

Sample	Carbon content <sup>a</sup> (%)	Aliphatic carbon content <sup>b</sup> (%)
CMC water	56.2	6.0
CMC C <sub>12</sub> TAB (0.02%)	57.4	7.7
CMC C <sub>12</sub> TAB (0.05%)	57.2	7.7
CMC C <sub>12</sub> TAB (0.1%)	57.4	9.5
CMC C <sub>14</sub> TAB (0.1%)	58.3	10.1
CMC C <sub>16</sub> TAB (0.1%)	58.1	11.4

CMC used: ZSB-16, 1% added on fibers

TAB, trimethylammonium bromide

<sup>a</sup>From wide spectrum

<sup>b</sup>From high-resolution regional spectrum

## Conclusions

CMC and cationic surfactants open up new possibilities for the modification of cellulosic fibers and their paper product properties. The main advantages indicated by these preliminary experiments are good internal strength of the paper.

Cationic surfactants can be easily attached to the surface of CMC-modified anionic fibers. Surprisingly, this treatment can substantially improve the internal strength of the prepared handsheets. Strong fibril bridges between the fibers observed in the ESEM images may partly explain the increased bonding strength. When salt was added before the pulps were formed into sheets, the tensile strength and density of the sheets stayed at quite a high level, even if the internal strength decreased dramatically. Further studies are necessary to explain the interaction in the fiber–CMC–surfactant system and the reason why the strength properties are improved when CMC and surfactants are added.

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**Appendix 1.** Sheet properties of beaten softwood pulp with and without sorbed carboxymethyl cellulose (CMC) (degree of substitution 0.32) on the surface and the effect of the added surfactants

Sample/added surfactant <sup>a</sup> (% on fibers)	Grammage (g/m <sup>2</sup> )	Thickness (μm)	Density (kg/m <sup>3</sup> )	Light-scattering coefficient (m <sup>2</sup> /kg)	Tear index (Nm <sup>2</sup> /kg)	Tensile index (Nm/g)	Internal strength (J/m <sup>2</sup> )
REF C <sub>10</sub> TAB							
0	62.8	102	617	22.3	21.2	52.4	255.1
0.02	63.8	103	621	22.4	21.1	48.9	234.7
0.1	63.0	102	616	22.4	21.2	51.2	240.6
0.2	63.9	101	634	22.2	24.0	53.0	263.3
CMC C <sub>10</sub> TAB							
0	67.3	103	653	20.2	12.7	73.6	493.4
0.02	65.1	106	617	22.2	15.8	62.8	354.3
0.1	64.1	102	627	21.9	15.0	63.4	446.6
0.2	64.3	97.8	657	21.1	13.1	70.9	488.3
REF C <sub>12</sub> TAB <sup>b</sup>							
0	65.0	104	626	21.8	21.1	56.2	267.9
0.02	64.5	101	640	21.2	18.4	69.4	264.6
0.05	65.2	101	644	21.3	20.9	58.2	281.2
0.1	64.5	102	634	21.5	19.2	56.9	281.4
0.15	65.3	100	651	21.3	20.1	57.7	273.6
0.2	64.8	101	644	21.6	18.9	61.3	291.1
CMC C <sub>12</sub> TAB <sup>b</sup>							
0	62.2	99.2	627	20.6	12.6	85.3	466.5
0.02	64.4	95.5	674	19.4	10.9	87.6	589.5
0.05	65.4	94.8	689	19.3	11.5	87.3	663.3
0.1	64.3	93.8	685	18.5	10.8	84.6	706.6
0.15	63.3	94.2	673	19.2	11.4	88.7	717.5
0.2	65.9	95.3	691	18.4	10.1	82.5	735.5
REF C <sub>12</sub> TAB+Salt							
0	64.4	106	608	22.8	20.7	52.1	250.4
0.1	64.4	106	610	22.6	20.5	46.7	235.1
0.2	63.8	103	621	22.3	20.9	50.3	256.3
CMC C <sub>12</sub> TAB+Salt							
0	65.5	99.8	656	20.2	11.2	80.0	484.7
0.1	64.9	102	635	21.2	12.2	81.0	453.9
0.2	64.0	100	637	20.9	13.5	76.6	478.8
REF C <sub>14</sub> TAB							
0	62.8	102	617	22.3	21.2	52.4	255.1
0.02	66.2	105	629	22.1	19.4	59.8	262.0
0.1	68.9	101	683	20.0	18.2	57.4	308.1
0.2	64.4	103	627	21.9	21.6	51.1	263.7
CMC C <sub>14</sub> TAB							
0	67.3	103	653	20.2	12.7	73.6	493.4
0.02	65.3	97	673	19.6	10.6	79.1	575.3
0.1	67.0	102	659	19.5	13.0	60.1	531.7
0.2	65.7	101	648	20.8	14.2	66.1	389.2
REF C <sub>16</sub> TAB							
0	62.8	102	617	22.3	21.2	52.4	255.1
0.02	63.7	101	630	21.5	19.2	54.8	265.0
0.1	61.5	96.8	636	22.1	18.0	57.5	293.6
0.2	64.0	104	617	22.8	22.1	48.4	242.7
CMC C <sub>16</sub> TAB							
0	67.3	103	653	20.2	12.7	73.6	493.4
0.02	65.6	97	676	20.0	11.3	83.2	548.7
0.1	67.8	102	666	19.6	12.2	67.2	518.7
0.2	67.2	108	623	21.6	18.8	55.7	377.8

<sup>a</sup> Sample codes: REF, no CMC added; CMC, CMC-treated pulp; Salt, 0.05 M NaCl added

<sup>b</sup> Second sorption batch